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EP-A- 0 134 267
BE-A- 536 819

Journal of the Textile Institute, Proceedings,
vol. 47, 1956, A.N. Davidson et al.:
"Shrink-resisting wool: some novel features
and the description of a new process",
pages 685-707; see page 687, no.3; page 691

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Journal of the Society of Dyers and Color-
ists, vol. 57, 1941, W.R. Middlebrook et
al.: "The application of enzymes to the pro-
duction of shrinkage-resistant wool and
mixture fabrics", pages 137-144

Textil-Praxis, vol. 18, no. 3, March 1963, E.P.
Frieser: "Das Filzfreilausrüsten von Wolle",
pages 236-237

Description

The present invention relates to a process for the production of wool and animal hairs with a low-in-felt or felt-free finish and to the wool or animal hairs so obtained.

To obtain felt-free wool has been a problem for many years and many methods including enzymatic treatments have been proposed to solve this problem. A review of such methods has been published by E.P. Frieser in *Textil-Praxis*, 18 - (1963, 03), pages 236 - 240 and he refers back to articles by W.R. Middlebrook and H. Phillips in *J. Soc.Dyers and Colorists*, 57 (1941), pages 137 - 144 and A.N. Davidson and R. Preston in *J. Text. Inst.* 47 (1956), pages 685 - 707 (also described in BE - A - 536 819). Although not always as explicitly stated as in EP - A - 0 134 267, the object of these enzymatic treatments was to achieve a complete descaling of the wool, i.e. that the outer surface of the fibres is totally removed and the character of the fibres changed in such a way that the natural aspect of the wool is lost.

The object of the present invention is to produce wool and animal hairs which keep their natural aspect and still have scales, but are low-in-felt or felt-free. This object is achieved by an enzymatic treatment which, in contrast to the known treatments, is superficial and short but effective to obtain a product that can be washed without negative consequences in ordinary household washing machines. A reliable method to differentiate this product from natural wool is the IWS Test Method 31, published by the International Wool Secretariate. Whereas the untreated fibres start to felt at the latest after 3 cycles of the described 7 A washes, the enzymatically treated wool according to the invention can stand at least 5 of these cycles without felting.

Another method to determine whether the wool fibres can be called felt-free is the well known Cubex-Test according to IWS Test Method 185, in which the shrinkage properties of wool are determined by treatment for one hour in cube form in a standardised washing appliance. In this test the wool should have an area shrinkage of $\leq 10\%$ after a Cubex test lasting at least one hour. By area shrinkage is understood the sum of the % shrinkage in length and of the % shrinkage in width. This corresponds to about 15-20 machine washes at high speed in a domestic washing machine without shrinkage or without significant alteration to the surface and shape.

Furthermore, the yarn strength of the treated wool should, compared with untreated wool, be lost by less than 15 % and the elongation should deteriorate by less than 20 %.

The invention, therefore, relates to a process for the production of wool or protein containing animal hair, which have a low-in-felt or felt-free finish defined by the following properties:

- a) an area shrinkage (sum of the % shrinkage in length and the % shrinkage in width) of $\leq 10\%$ after a Cubex test lasting at least one hour or after 5 cycles 7 A according to IWS TM 31,
- b) a loss of yarn strength, compared with untreated wool or hair, of less than 15 %, and
- c) an elongation which deteriorates by less than 20 %,

comprising an oxidative pretreatment of the wool or hair, followed by treatment thereof with a protease, characterised in that the oxidative pretreatment is a chlorination using active chlorine, that

- d) the wool or the hair is contacted with the protease by means of impregnation from a short bath having a liquor-to-goods ratio in the range of 1:0.7 to 1:5;

that the wool or hair is squeezed out and

- e) the wool or hair, with the protease from the bath still thereon, is subjected to thermal treatment at a temperature between room temperature (20 °C) and 140 °C with high frequency (HF) waves for up to one hour.

By protease is understood any protein-splitting enzyme. Suitable proteases are enzymes recovered from bacteria, for example *esperase*, *pro-nase E*, *protease P*, *subtilysin*, *thermolysin*, as well as enzymes from animal or plant origin, for example *trypsin*, *pepsin*, *pancreatin* or *bromelain*. Mixtures of various enzymes can also be used. These proteases are available commercially. Preferred proteases for the process according to the invention are the animal and vegetable enzymes, especially *bromelain*.

The effectiveness of the enzyme employed can be increased by adding specific activators such as cysteine, dithioerythrol, dithiothreitol or mercaptoethanol. Further additives, such as salts which are known for stabilising enzymes, can also be used, e.g. calcium or zinc chloride. These salts are employed in a quantity which corresponds to the enzyme.

Treatment of the wool or hair with a protease is effected by means of impregnation from a short bath, for example by padding, spraying, coating or printing. The protease may be applied from an aqueous medium or from organic solvent, or also as a paste or foam. The liquor-to-goods ratio is conveniently in the range 1:0.7 to 1:10, preferably 1:1 to 1:5.

Application of the protease is preferably effected at a temperature between room temperature and 60 °C. The treatment liquor or paste is preferably set at a pH value between 4 and 9, specially

5-7, using a commercial buffer.

The protease is conveniently used in a quantity of 0.1 to 5 %, calculated on the dry weight of the wool. When applied by means of impregnation, the protease is used in a quantity of 0.1 to 2%, corresponding to an enzyme activity of 400 to 1500 CDU(casein digesting unit)/mg. Preferably a quantity of 0.5 to 1 % is used.

Directly after the enzymatic treatment, the wool or hair is either left to dwell and/or undergoes thermal treatment. The dwelling period may last from a short interim period to several hours, with partial or complete drying of the goods. Depending on the temperature, the thermal treatment may take place for a few minutes up to several hours, optionally until the wool is dry. High frequency (HF) waves are used for the thermal treatment. In the HF drier, the wool or hair is conveniently treated at about 100-102°C between 10 minutes and 1 hour. The conditions for the dwelling period or the thermal treatment are chosen such that the wool obtained has the desired properties, and preferably such that the enzyme is simultaneously deactivated at the end of the treatment. Any enzyme that is still active can also be deactivated by known methods after treatment.

The wool or hair is then washed and dried, and further processed.

The process according to the invention may be used both for wool and for other protein-containing animal hairs. The fibre material may exist in various stages of processing, e.g. in the form of flocks, tops and roving, yarn, knitted goods, woven goods, non-wovens or felts. The wool may be used for the process according to the invention in the raw or pre-treated state.

In order to attain certain effects and/or to optimise the effect of the protease, it may be convenient to carry out special pre-treatments prior to the enzymatic treatment. Suitable pre-treatments for wool or hair may be for example oxidative treatments, e.g. with hydrogen peroxide, optionally in the presence of a stabiliser, with potassium permanganate, Caro's acid, chlorine or chlorine-containing compounds such as chlorine gas, hypochlorites or organic chlorine carriers, or with ozone.

After the pre-treatment, the wool or hair is rinsed and dried.

In a preferred feature of the process according to the invention, the wool or hair is chlorinated by oxidation and then treated with a protease.

The oxidative chlorination of the wool or hair is preferably carried out using active chlorine, e.g. in the form of chlorine gas in water or in the form of sodium hypochlorite with hydrochloric acid. This pre-treatment may be carried out by known methods. The wool or hair preferably undergoes

mild chlorination. The wool or hair is preferably chlorinated with a quantity of 0.1 to 2% of active chlorine, calculated on the dry weight of the wool or hair. This treatment advantageously takes place at a pH of 2-3 for 1 to 10 seconds. Chlorination is preferably effected at a temperature of between 10 and 30°C.

After the pre-treatment, in order to attain the desired enzymatic effect, it is advantageous for the wool or hair to be free from residual pre-treatment agents and to have a pH in a neutral range.

After chlorination, the fibre material is treated so as to be free from residual chlorine, and is subsequently or simultaneously neutralised. The chlorine present on the fibre or in the fibre is removed by treatment with a reducing agent, for example sodium bisulphite, sodium sulphite etc. Neutralisation is advantageously carried out with an alkaline compound, for example an alkali metal carbonate.

Depending on the chosen conditions of the process, with or without pre-treatment, the scaly layer of the wool or hair is partly or only slightly changed or activated. As a result of the enzyme treatment, wool or hair is obtained which has reduced felt behaviour and does not provoke problems during further processing (spinning, bleaching, dyeing) and during usage and washing of the articles made therefrom. The wool which is treated in accordance with the invention has a soft and, which is particularly advantageous, natural woolly handle. When it is chlorinated as tops and is then treated enzymatically as mentioned above, an especially soft wool or hair is produced. The dyeing behaviour of the wool or hair which is treated according to the invention and the fastness properties of the dyed wool or hair are also not adversely affected, on the contrary they are considerably improved.

The following examples illustrate the invention. All percentages are by weight and all temperatures are given in Centigrade.

EXAMPLE 1

Wool tops are firstly padded for 3 seconds at a temperature of 10-20° on a split paddler for tops with chlorine water containing 0.4 % active chlorine. The wool is subsequently rinsed, then treated for 45 seconds with liquor containing 4 g/l sodium carbonate and 1 g/l sodium bisulphite, and washed twice.

Wool tops are padded at 40° with an aqueous liquor which is buffered to pH 6.0 and contains 0.5 % espase [Bac. lich., obtainable from Novo (Denmark)] calculated on the dry weight of the tops, and then squeezed out to a pick-up of 50 %.

The impregnated tops are subsequently left to dwell for an interim period and then treated for 30 minutes in a HF drier at 100-102°. After this treatment, the tops are washed out and then dried.

A soft wool which is low in felt and which can be spun with little waste is obtained.

A protease such as pancreatin can be used in example 1 instead of the esperase. A wool with a soft woolly handle and shrink-resistant properties is obtained.

Example 1 is repeated using, instead of 0.5 % of esperase, 0.5 % of bromelain.

Wool with a soft woolly handle and shrink-resistant properties is obtained.

Claims

1. Process for the production of wool, or protein-containing animal hair, which have a low in felt or felt-free finish defined by
 - a) an area shrinkage (sum of the % shrinkage in length and the % shrinkage in width) of $\leq 10\%$ after a Cubex test of at least one hour or after 5 cycles 7 A according to IWS TM 31,
 - b) a loss of yarn strength, compared with untreated wool or hair, of less than 15%; and
 - c) an elongation which deteriorates by less than 20 %, comprising an oxidative pretreatment of the wool or hair, followed by treatment thereof with a protease, characterised in that the oxidative pretreatment is a chlorination using active chlorine, that
 - d) the wool or the hair is contacted with the protease by means of impregnation from a short bath having a liquor-to-goods ratio in the range of 1:0.7 to 1:5 that the wool or hair is squeezed out and
 - e) the wool or hair, with the protease from the bath still thereon, is subjected to thermal treatment at a temperature between room temperature (20°C) and 140°C with high frequency (HF) waves for up to one hour.
2. Process according to claim 1, characterised in that the protease used is esperase, pronase E, protease P, subtilysin, thermolysin, trypsin, pepsin, pancreatin or bromelain.
3. Process according to claims 1 or claim 2, characterized in that the protease is used in a quantity of 0.1 to 5%, calculated on the dry weight of the wool or hair.

4. Enzymatically treated, resin free wool or animal hair with substantially unchanged scaly layer having the following properties:
 - a) an area shrinkage (sum of the % shrinkage in length and the % shrinkage in width) of $\leq 10\%$ after a Cubex test of at least one hour or after 5 cycles 7 A according to IWS TM 31,
 - b) a loss of yarn strength, compared with untreated wool or hair, of less than 15%; and
 - c) an elongation which deteriorates by less than 20%.

15 Patentansprüche

1. Verfahren zur Herstellung von Wolle oder proteinhaltigen Tierhaaren mit einer leicht filzenden oder filzfreen Ausrüstung, die durch
 - a) eine Flächenschrumpfung (Summe der prozentuellen Längeschrumpfung und der prozentuellen Breiteschrumpfung) von $\leq 10\%$ nach einem Cubextest von mindestens einer Stunde oder nach 5 Zyklen 7 A gemäss IWS TM 31,
 - b) einen Verlust der Garnfestigkeit im Vergleich zur unbehandelten Wolle oder Haaren von weniger als 15 %,
 - c) eine Dehnung, die weniger als 20 % verschlechtert, definiert ist, durch eine oxidative Vorbehandlung der Wolle oder Haare, gefolgt durch eine Behandlung mit einer Protease, dadurch gekennzeichnet, dass die oxidative Vorbehandlung eine Chlorierung mit aktivem Chlor ist, dass
 - d) die Wolle oder Haare durch Imprägnierung in einer kurzen Flotte mit einem Flottenverhältnis im Bereich von 1:0,7 bis 1:5 mit der Protease in Kontakt gebracht wird, dass die Wolle oder Haare abgequetscht werden und
 - e) die Wolle oder Haare mit der Protease aus dem Bad darauf, bis zu einer Stunde einer thermischen Behandlung bei einer Temperatur zwischen Raumtemperatur (20°C) und 140°C mit Hochfrequenz (HF)-Wellen unterworfen wird.
2. Verfahren gemäss Anspruch 1, dadurch gekennzeichnet, dass die verwendete Protease Esperase, Pronase E, Protease P, Subtilysin, Thermolysin, Trypsin, Pepsin, Pancreatin oder Bromelain ist.
3. Verfahren gemäss Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Protease in einer Menge von 0,1 bis 5 %, berechnet auf das

Trockeng wicht der Woll oder Haare, verwendet wird.

4. Enzymatisch behandelte, harzfreie Woll oder Tierhaare mit weitgehend unveränderter Schuppenschicht, die folgende Eigenschaften aufweisen:

- a) eine Flächenschrumpfung (Summe der prozentuellen Längeschrumpfung und der prozentuellen Breiteschrumpfung) von ≤ 10 % nach einem Cubextest von mindestens einer Stunde oder nach 5 Zyklen 7 A gemäss IWS TM 31,
- b) einen Verlust der Garnfestigkeit im Vergleich zur unbehandelten Wolle oder Haaren von weniger als 15 %,
- c) eine Dehnung, die weniger als 20 % verschlechtert.

Revendications

1. Procédé de préparation de laine ou de poils d'animaux, faiblement feutrables ou infeutrables et définis par

- a) un rétrécissement de surface (somme du % de rétrécissement dans la longueur et du % de rétrécissement dans la largeur) $\leq 10\%$ après un essai Cubex d'au moins 1 heure ou après 5 cycles 7A selon IWS TM 31,

- b) une perte de résistance du filé, par rapport à la laine ou aux poils non traités, inférieure à 15% et

- c) un allongement qui se détériore de moins de 20%,

comprenant un pré-traitement oxydant de la laine ou des poils suivi par leur traitement avec une protéase,

caractérisé en ce que le pré-traitement oxydant est un chlorage utilisant du chlore actif, en ce que

- d) la laine ou les poils sont mis en contact avec la protéase par imprégnation en bain court avec un rapport de bain de 1:0,7 à 1:5,

en ce que la laine ou les poils sont exprimés et en ce que

- e) la laine ou les poils, avec la protéase provenant du bain et encore présente sur eux, sont soumis pendant une heure maximum à un traitement thermique à une température comprise entre la température ambiante (20° C) et 140° C avec des ondes à haute fréquence (HF).

2. Un procédé selon la revendication 1, caractérisé en ce que la protéase utilisé est l'espérase, la pronase E, la protéase P, la

subtilysine, la thermolysine, la trypsine, la pepsine, la pancréatine ou la bromélaïne.

3. Un procédé selon la revendication 1 ou 2, caractérisé en ce que la protéase est utilisée en une quantité comprise entre 0,1 et 5% en poids par rapport au poids de la laine ou des poils à l'état sec.

4. Laine ou poils d'animaux exempts de résine qui ont été traités par des enzymes, qui comportent une couche d'écailles essentiellement inchangée et qui présentent les propriétés suivantes:

- a) un rétrécissement de surface (somme du % de rétrécissement dans la longueur et du % de rétrécissement dans la largeur) $\leq 10\%$ après un essai Cubex d'au moins 1 heure ou après 5 cycles 7A selon IWS TM 31,

- b) une perte de résistance du filé, par rapport à la laine ou aux poils non traités, inférieure à 15% et

- c) un allongement qui se détériore de moins de 20%.